Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplemental Information

Evaluating the effects of OH-group on the Ni surface on low-temperature steam reforming in an electric field

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Reaction apparatus

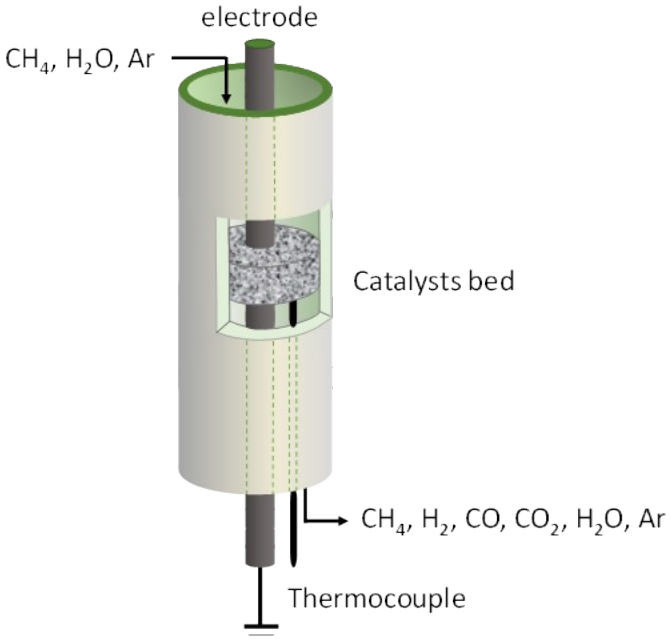

Fig. S1 Reaction apparatus

Additional information on the calculation of the reaction rate and selectivity.

The reaction rate was calculated using the amount of CO and CO_2 produced (r_{CO+CO2}), and the CH_4 conversion and CO_2 selectivity were calculated using the following equations 1 – 3.

$$r_{CO+CO2}\ (\text{mmol min}^{-1}) = F_{CO,\,out} + F_{CO2,\,out} \quad \text{eq. 1}$$

$$CH_4\ \text{conversion}\ (\%) = \frac{F_{CO,\,out} + F_{CO2,\,out}}{F_{CH4,\,in}} \times 100 \quad \text{eq. 2}$$

$$CO_2\ \text{Selectivity}\ (\%) = \frac{F_{CO2,\,out}}{F_{CO,\,out} + F_{CO2,\,out}} \times 100 \quad \text{eq. 3}$$

In addition, the power efficiency (ΔH/EP) was calculated by the following equations 4 –

6. Here EP denotes the electric power consumption.

$$\Delta rH\ (J\ s^{-1}) = r_{CO} \times \Delta HCO + rCO2 \times \Delta HCO2\_ \quad r_{CO} \times \Delta HCH4\ \_(rCO + 2rCO2) \times \Delta HH2O \qquad \text{eq. 4}$$

$$EP\ (J\ s^{-1}) = I \times V \qquad \text{eq. 5}$$

$$\Delta H/EP\ (\%) = \Delta rH/EP \times 100 \qquad \text{eq. 6}$$

ΔrH / J s^{-1}	: Reaction enthalpy
I / mA	: Direct current
V / kV	: Response voltage
EP /J s^{-1}	: Input power
ΔH_{CO} / kJ mol^{-1}	: Standard enthalpy of formation of CO = -110.57kJ mol^{-1}
ΔH_{CO2} / kJ mol^{-1}	: Standard enthalpy of formation of CO_2 = -393.51kJ mol^{-1}
ΔH_{CH4} / kJ mol^{-1}	: Standard enthalpy of formation of CH_4 =-74.5kJ mol^{-1}
ΔH_{H2O} / kJ mol^{-1}	: Standard enthalpy of formation of H_2O =-241.82kJ mol^{-1}

The stability of catalyst-activity was confirmed on a Ni-doped YSZ catalyst for 5 hours. As a pretreatment, a mixed-gas flow of H_2: H_2O: Ar = 60-*x*: *x*: 60 (*x* = 30, 60, total flow: 120 SCCM) was applied at a furnace temperature of 873 K, 1 hour. Reaction conditions, and reaction apparatus were the same as activity tests.

Other characterization

XRD

Powder X-ray diffraction (XRD; Smartlab III; Rigaku Corp.) was used to conduct for analysis of the physical structure of each sample. These were observed at 40 kV, and 40 mA with Cu-*K*α radiation. Results are summarized in Fig. S4.

Specific surface area of the catalyst by the Brunauer-Emmett-Teller (BET) method

To determine the specific surface area of the catalysts after the ER activity test with different pretreatments, BET measurements were performed using an automatic

specific surface area measuring device (Gemini VII, MicrotracBEL). About 50 mg of catalyst was weighed by the weight loss method and purged with He gas at a holding temperature of 473 K for 1 hour as a pretreatment. Then N_2 gas flowed through the catalyst, N_2 was adsorbed into the pores of the catalyst, and the amount of N_2 adsorbed was measured. The specific surface area of the catalyst was calculated from the adsorption amount. The following BET adsorption isotherm equations 7 and 8 were used for the calculation.

$$V\,(\mathrm{mol}) = \frac{c \times V_m \times p}{(p - p_0)((c-1)p + p_0)} \qquad \text{eq. 7}$$

$$A\,(\mathrm{m^2\,g^{-1}}) = V_m \times {}^{N_A}\!/_{28} \times \delta N2 \times 10^{-18} \qquad \text{eq. 8}$$

V / mol	: The amount of N_2 adsorption
C / -	: Parameters related to the heat of adsorption
V_m / mol	: Absorption capacity of the single molecular layer
P / Pa	: Balanced suction pressure
p_0 / Pa	: Saturated vapor pressure
A / $m^2\,g^{-1}$	: Specific surface area
N_A / mol^{-1}	: Avogadro's number
δ_{N2} / nm^2	: Cross-sectional area per molecule of N_2 (0.162 nm^2)

Measurement of the amount of adsorbed water

The previous studies[7, 9] has shown that the amount of water adsorbed on the carrier is important for improving proton conductivity, which is an important factor in ER. Therefore, we measured the amount of adsorbed water in each pretreatment. The amount of adsorbed water was estimated by thermogravimetric analysis (TGA-50,

Shimadzu). 50 mg of Ni-doped YSZ catalyst was first pretreated with a flow of H_2: H_2O: Ar = 5: 5: 90, 10: 0: 90 (total flow: 100 SCCM) at 873 K for 1 hour with the ramping rate of 10 K min^{-1}. The samples were then heated to 873 K for 1 hour with following gas, H_2O: Ar = 1: 49 (total flow: 100 SCCM). After the weight was stabilized, each sample was cooled to 323 K and then heated again to 873 K at a ramping rate of 5 K min^{-1}. The adsorption and desorption of water molecules were checked by observing the weight change during this operation, and the adsorption amount of water was calculated using the following equation 9. For BET, the values calculated using the method described above were used. Results are summarized in Table S4.

$$W_{water}\square(\mathrm{g\ m^{-2}}) = \frac{W_{473\ K} - W_{873\ K}}{A \times m} \quad \ldots \text{eq. } 9$$

W_{water} / g m^{-2}	: The adsorption amount of water molecule per unit area at 473 K
$W_{473\ K}\square$ / g	: Weight loss at 473 K
$W_{873\ K}\square$ / g	: Weight loss at 873 K
A / m^2 g^{-1}	: Specific surface area
m / g	: Initial weight of the catalyst

Activity under different pretreatment conditions with a different catalyst

It was investigated whether these differences in activity in the ER due to pre-treatment also appear in other catalysts. Here, ER tests were conducted using a 1.0wt%Pt/CeO_2 catalyst (the preparation method is described in ESI), which is already known to be highly active in methane steam reforming, with different pre-treatment composition ratios. As shown in Fig. S5, no difference in ER activity was observed with different pre-treatment conditions.

Compared to the Ni-YSZ catalyst in 3.1, the change in activity due to different pre-treatments with hydrogen and steam is specific to the Ni-doped YSZ catalyst. The difference in activity due to different pre-treatments is not due to non-steady-state surface conditions, as it persists over a long period of time; YSZ can retain protons and water molecules at grain boundaries and inner surfaces, resulting in a hierarchical structure of hydroxyl and water molecules.[9] In YSZ, proton conduction also occurs in the bulk interior. Therefore, the effect of this pre-treatment may also contribute to the bulk interior, resulting in a specific ER-active behaviour due to pre-treatment changes.

References (cited in this ESI)

7) A. Takahashi, R. Inagaki, M. Torimoto, Y. Hisai, T. Matsuda, Q. Ma, J.G. Seo, T. Higo, H. Tsuneki, S. Ogo, T. Nordy and Y. Sekine, RSC Adv., 2020, **10**, 14487-14492.

9) S. Ø. Stub, E. Vøllestad, and T. Norby, J. Phys. Chem. C., 2017, **121**(23), 12817-12825.

Table S1 Results of activity tests conducted with the EF: catalyst, $Zr_{0.65}Y_{0.05}Ni_{0.3}O_2$; catalyst amount: 80 mg; pre-treatment, H_2: H_2O: Ar=*x*: (60-*x*): 60 (*x*=0, 12, 30, 48, 60), or Ar only; reaction gas flow, CH_4: H_2O: Ar = 1: 2: 7; total 120 SCCM; furnace temp.: 473 K; current: 3–9 mA.

Pretreatment H_2/H_2O	Current / mA	r(CO+CO2) / mmol min^{-1}	Voltage / kV	EP / W	Cat. temp. / K	Conv. / %
60/0	3	0.0721	0.327	0.982	517.0	10.4
	5	0.0931	0.267	1.33	529.2	13.4
	3	0.0712	0.318	0.955	514.2	10.2
	7	0.0973	0.209	1.46	524.4	14.2
	5	0.0899	0.250	1.25	525.9	12.9
	7	0.105	0.208	1.45	534.1	15.2
	9	0.113	0.182	1.64	540.4	16.3
48/12	7	0.0975	0.171	1.20	507.7	12.0
	5	0.0976	0.234	1.17	505.9	12.0
	3	0.0878	0.323	0.970	498.6	10.8
	5	0.101	0.226	1.13	507.0	12.5
	7	0.122	0.233	1.63	528.4	15.0
	9	0.135	0.210	1.89	537.8	16.6
	7	0.127	0.245	1.71	530.3	15.7
	5	0.117	0.277	1.39	519.4	14.4
	3	0.0965	0.358	1.08	505.2	11.9
	5	0.116	0.288	1.44	521.0	14.3
	9	0.136	0.192	1.73	535.8	16.8
30/30	9	0.126	0.144	1.29	532.6	14.4
	7	0.152	0.218	1.53	547.8	17.4
	3	0.135	0.413	1.23	536.4	15.5
	5	0.154	0.317	1.59	552.1	17.7
	7	0.176	0.256	1.79	564.0	20.2
	9	0.200	0.247	2.22	578.5	22.9
	7	0.191	0.288	2.02	572.9	21.9
	5	0.161	0.348	1.74	558.8	18.5
	9	0.164	0.216	1.94	545.5	19.7
	7	0.162	0.262	1.83	543.2	19.5
	5	0.139	0.324	1.62	534.1	16.8
	3	0.110	0.418	1.25	521.1	13.2
	5	0.136	0.314	1.57	531.8	16.4
	9	0.166	0.220	1.98	546.7	20.0
	9	0.137	0.220	1.98	542.0	22.6
	9	0.169	0.248	2.23	544.3	27.7
	9	0.149	0.226	2.03	540.5	24.5
	9	0.147	0.232	2.09	542.5	24.3
	9	0.149	0.225	2.02	539.1	24.5
	9	0.149	0.230	2.07	540.7	24.5
	9	0.149	0.232	2.08	541.2	24.6
	9	0.149	0.233	2.10	542.1	24.5
	9	0.151	0.239	2.15	543.5	24.9
	9	0.153	0.248	2.23	546.6	25.2
	9	0.156	0.245	2.20	546.4	25.6
	9	0.153	0.245	2.21	548.1	25.1
	9	0.145	0.224	2.02	543.9	23.9
	9	0.148	0.225	2.03	541.8	24.4
	9	0.152	0.251	2.26	545.6	25.0
12/48	7	0.100	0.170	1.19	484.9	13.0
	3	0.0779	0.252	0.755	471.6	10.1
	5	0.112	0.248	1.24	486.0	14.4
	7	0.132	0.224	1.57	495.7	17.1
	9	0.147	0.184	1.66	505.5	19.0
	9	0.145	0.205	1.85	511.1	18.8
	3	0.100	0.385	1.15	486.9	13.0
	3	0.0959	0.328	0.984	480.3	12.4
0/60	5	0.0651	0.251	1.26	522.9	7.98
	3	0.0532	0.332	0.997	512.1	6.52
	5	0.0800	0.252	1.26	521.8	9.81
	7	0.0831	0.212	1.48	534.3	10.2
	9	0.0891	0.165	1.49	529.3	10.9
	7	0.0715	0.188	1.32	522.3	8.76
	5	0.0626	0.208	1.04	515.4	7.67
	7	0.0600	0.153	1.07	512.6	7.36
Ar only	7	0.123	0.290	2.03	629.7	14.2
	5	0.0958	0.350	1.75	514.9	11.1
	3	0.0717	0.411	1.23	503.7	8.33
	5	0.100	0.350	1.75	518.4	11.7
	7	0.121	0.302	2.10	530.4	14.1
	9	0.133	0.220	1.98	534.3	15.5
	5	0.112	0.380	1.90	524.6	13.0

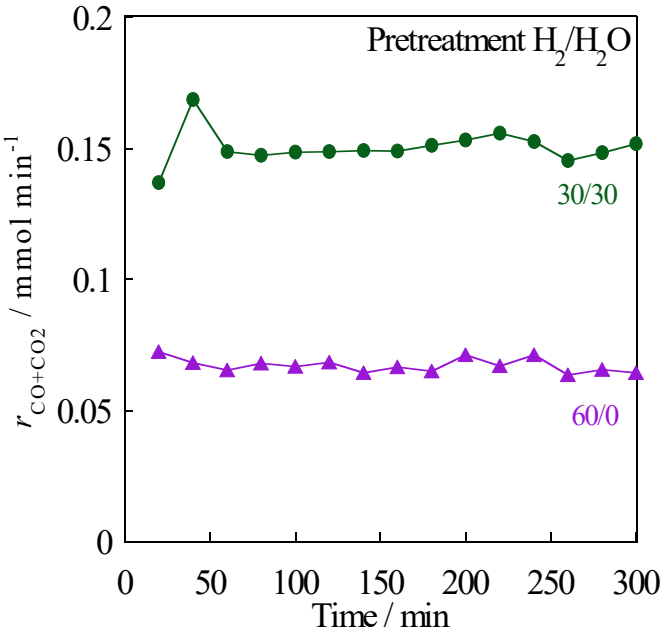

Fig. S2 The result of activity test; catalyst, $Zr_{0.65}Y_{0.05}Ni_{0.3}O_2$, Pretreatment, H_2: H_2O: Ar=*x*: (60-*x*): 60 (*x*=30, 60); catalyst mount, 80 mg; reaction gas flow, CH_4: H_2O: Ar= 1: 2: 7, total flow rate: 120 SCCM; furnace temp.: 473 K; imposed current: 9 mA.

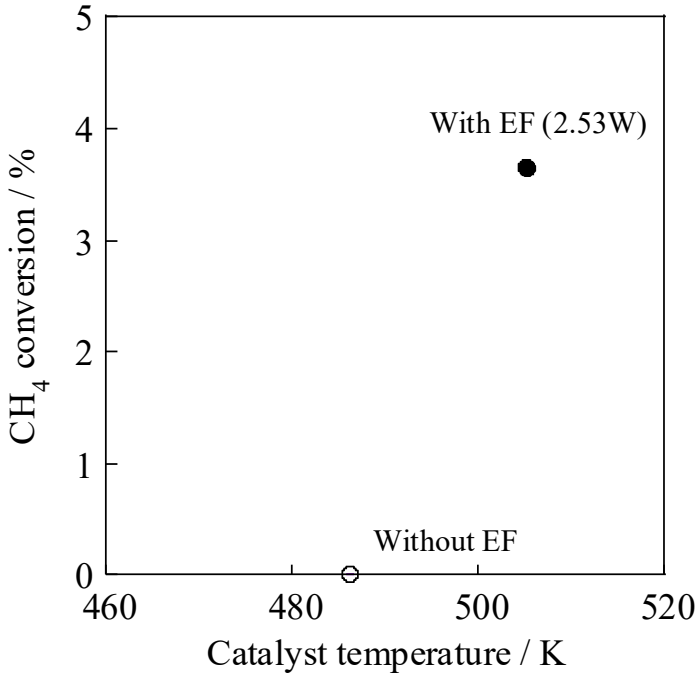

Fig. S3 The result of activity test with and without electric field over $Ni(OH)_2$ without catalyst support; catalyst amount, 50 mg; reaction gas flow, CH_4: H_2O: Ar = 1: 2: 7, total flow rate 120 SCCM; furnace temp. 473 K.

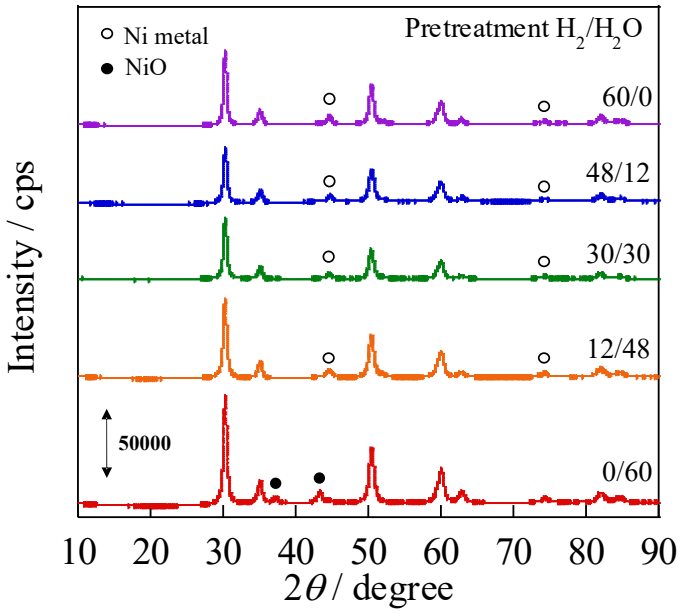

Fig. S4 The XRD patterns after run with EF; catalyst, $Zr_{0.65}Y_{0.05}Ni_{0.3}O_2$, pretreatment, H_2: H_2O: Ar=*x*: (60-*x*) : 60 (*x*=0, 12, 30, 48, 60); amount, 80 mg; flow, CH_4: H_2O: Ar = 1: 2: 7, total 120 SCCM; furnace temp. 473 K; imposed current, 3 – 9 mA.

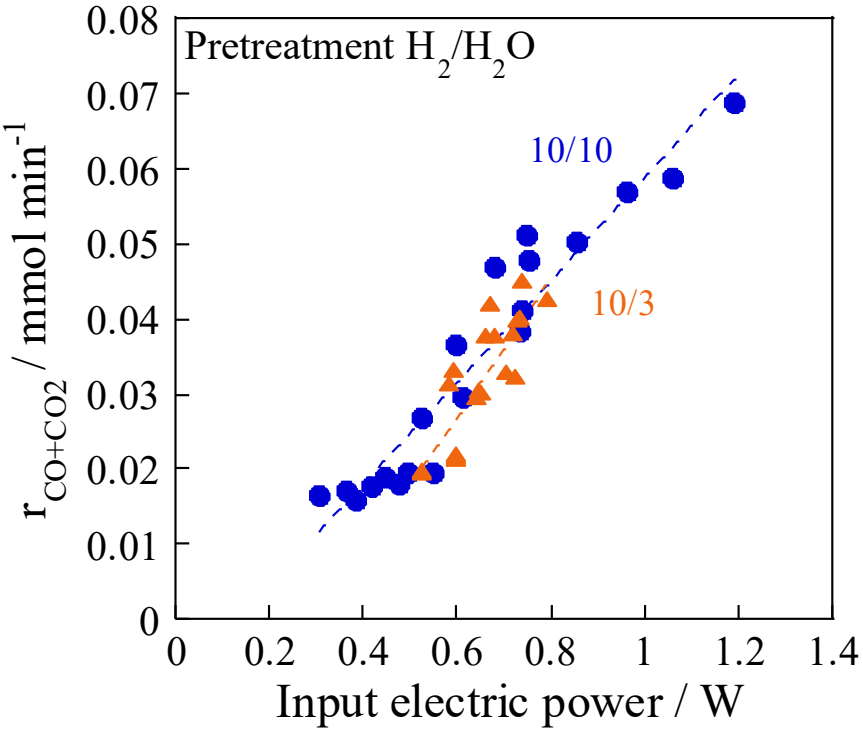

Fig. S5 The results of activity test; catalyst: 1.0 wt%Pt/CeO_2, pretreatment, H_2: H_2O: Ar=10: 3: 87 or 10: 10: 80; catalyst amount: 80 mg; reaction gas flow, CH_4: H_2O: Ar = 1: 2: 7, total flow rate: 100 SCCM; furnace temp. 473 K; imposed current, 3 – 9 mA.

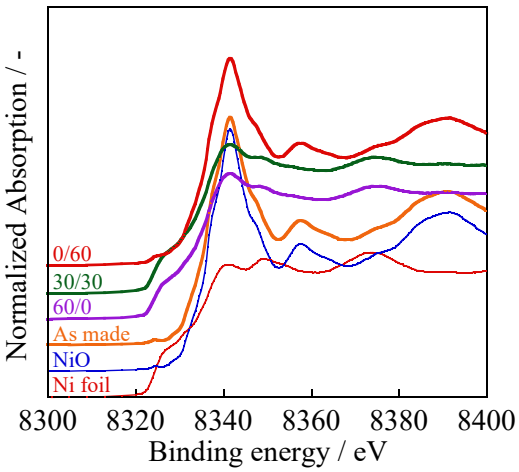

Fig. S6 Ni-*K* edge XANES spectra; catalyst, $Zr_{0.65}Y_{0.05}Ni_{0.3}O_2$ after ER test, pretreatment, H_2: H_2O: He=*x*: (60-*x*): 60 (*x*=0, 30, 60); catalyst amount: 80 mg; reaction gas flow, CH_4: H_2O: He = 1: 2: 7, total flow rate: 120 SCCM; furnace temp. 473 K; imposed current: 3 - 9 mA.

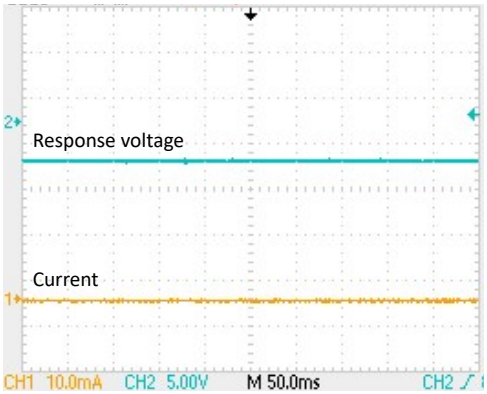

Fig. S7 Current and voltage waveforms; catalyst, $Zr_{0.65}Y_{0.05}Ni_{0.3}O_2$, pretreatment, H_2: H_2O: Ar=60: 0: 60; catalyst amount: 80 mg; reaction gas flow, CH_4: H_2O: Ar = 1: 2: 7, total flow rate: 120 SCCM; furnace temp. 473 K; applied electric power: about 1.5 W.

Table S2 Ni crystal size after run with EF; catalyst, $Zr_{0.65}Y_{0.05}Ni_{0.3}O_2$, pretreatment, H_2: H_2O: Ar=*x*: (60-*x*): 60 (*x*=30, 60); reaction gas flow, CH_4: H_2O: Ar = 1: 2: 7, total flow rate: 120 SCCM; furnace temp. 473 K; imposed current: 3 – 9 mA.

Samples (H_2/H_2O)	Ni crystal size / nm
30/30	22.3
60/0	20.1

Table S3 Specific surface area after run with EF; catalyst, $Zr_{0.65}Y_{0.05}Ni_{0.3}O_2$, pretreatment, H_2: H_2O: Ar=*x*: (60-*x*): 60 (*x*=30, 60); amount, about 50 mg; reaction gas flow, CH_4: H_2O: Ar = 1: 2: 7, total 120 SCCM; furnace temp.: 473 K; imposed current: 3 – 9 mA.

Samples (H_2/H_2O)	Specific surface area / $m^2\ g^{-1}$
30/30	13.2
60/0	13.9

Table S4 Amount of H_2O adsorption and coverage; catalyst, $Zr_{0.65}Y_{0.05}Ni_{0.3}O_2$, pretreatment, H_2: H_2O: Ar=5: 5: 90 or 10: 0: 90, total gas flow: 100 sccm, catalyst amount; about 50 mg.

Sample (H_2/H_2O)	Weight / g	Surface area / m^2	Unit H_2O adsorption / mg m^{-2}	Average unit H_2O adsorption / mg m^{-2}	Coverage / -	Average Coverage / -
5/5_1st	0.0460	0.467	0.510	0.457	2.84	2.62
5/5_2nd	0.0495	0.500	0.404		2.40	
10/0_1st	0.0400	0.404	0.715	0.725	3.45	3.55
10/0_2nd	0.0412	0.416	0.735		3.65	